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SYNTHESIS, GROWTH, STRUCTURAL, SPECTRAL, OPTICAL AND THERMAL PROPERTIES OF LITHIUM NITRATE DOPED THIOUREA CRYSTAL

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ABSTRACT

In the current work is concerned with the analysis of Thiourea Lithium Nitrate Crystals have been grown and distinct characterization techniques are examined from the slow evaporation way of low temperature solution growth method at room temperature with double distilled water. The design and search of high effective nonlinear optical crystals for ultraviolet and visible regions are very vital for material and laser processing. In differently the very low concentration impurity does not have any influence on the arrangement. The FT-IR is efficiently utilized to identify the functional groups within the synthesis chemical and it's been discovered that extending of molecules in particular frequencies. The optical transparency and also the lower cutoff wavelength at 285 nm were identified in the UV-Vis NIR spectrum. The Kurtz and Perry powder strategy at second harmonic generation evaluation proves that the crystal is a promising candidate for great optical properties. Thermal analysis reveals that the grown crystals were thermal stability up to 210° C.

KEYWORDS: Crystal Growth, Single and Powder XRD, FTIR, UV-Vis, NLO & TG/DTA

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Original Article

1. INTRODUCTION

Crystal grew now-a-days find areas which range from microelectronics, medical devices, communicating systems, laser and defense resources up into the space satellites and age. Crystal expansion of notable role of drama in the age of immense technological superiority attributing to the viability in significant area of the humankind namely science, medicine, technology, technology and strategies Regions of defense and Several crystals are utilized in piezo-electric, acoustic-optic, picture refractive, photograph elastic, electro-optical programs and radiation, sensors, laser hosts, parametric amplifiers transducers, harmonic generators etc.,

Development of crystals from aqueous solution is just one of those early procedures of crystal growth. This system of crystal growth is very well known in creation of several technologically significant crystals. The development of crystals with low temperature alternative involves months and sometimes years.

Light is distracted or postponed however, it frequency is unchanged. Non-linear optics: Optics of extreme light we're worried about the effects that light itself causes since it spreads through the medium.

In the current work, another NLO substance of different percentage of lithium nitrate doped thiourea crystals have been grown from aqueous solution by dividing double distilled water utilizing slow evaporation technique at room temperature. The grown crystals of different proportion (0.5:2M, 1.0:2M and 1.5:2M) were

harvested. It is concerned with the investigation of the Thiourea Lithium Nitrate Crystals growth and different characterization techniques are analyzed.

1.1. Materials

All reagents are analytically high purity of Thiourea (Merck 99%) and Lithium Nitrate (AR grade) were taken in different molar ratio 0.5:2M, 1:2M and 1.5:2M and dissolved in double distilled water.

Thiourea is a organosulfur compound Using the formula SC It's structurally like urea, except the oxygen molecule is replaced by a sulfur molecule and Thioureas are related to thioamides, eg. RC(S) NR2, where R is methyl, ethyl, etc., Thiourea is a reagent in organic synthesis.

Lithium nitrate is a natural compound together with the Formula LiNO3. It's the lithium salt of nitric oxide. It's made by Other group that I nitrates decompose otherwise, Forming the nitrite oxygen and salt. Due to its comparatively small size, the Lithium cation is quite polarizing, which simulates the creation of this oxide. Lithium nitrate can also be denser than water.

$4LiNO_3 + 2Li_2 O + 4 NO_2 + O_2$

1.2. Solubility

The solubility of lithium nitrate doped thiourea salts have been completed in a solvent of double distilled water in five fever (30 °C, 35 °C, 40 °C, 45 °C and 50 °C). The purified re-crystallized salts of TuLiNO3 were dissolved in double distilled water and all these alternatives are stored in an airtight container. Solubility analysis was completed with a magnetic stirrer and an electronic thermometer. The temperature was controlled with a voltage regulator connected to the magnetic stirrer (precision is ±0.01°C). At first, the answer was stored at room temperature and stirred consistently employing the magnetic stirrer for approximately three hours. It can be seen that the solubility $TuLiNO_3$ mixed solutions increases significantly with increasing temperature.

1.3. Synthesis

Lithium nitrate doped thiourea salts were synthesized by dissolving lithium nitrate and thiourea in various molar ranges (0.5:2M, 1:2M and 1.5:2M) by mixing in double distilled water at room temperature. The alternative of lithium ion was added into this solution of thiourea the mix had to be stirred vigorously to prevent precipitation of different stages. The TULiNO3 alternative was ready and kept at room temperature at a constant temperature bath having a precision of ± 0.01 °C with constant stirring to make sure continuing temperature immersion over the full quantity of this solution. The solution was stirred well for three hours constantly using magnetic stirrer, and was filtered by using Whattmann filter paper. These solutions are redistributed in three different beakers. These salts were purified by repeated recrystallization process by using double distilled water as solvent. The synthesized substances were purified by evaporation technique to obtain thiourea lithium nitrate mixed crystals of high quality, purification is an important steps. Hence, crystallizations were repeated for more than three times.

2. PREPARATION OF CRYSTAL GROWTH

The solutions were prepared by dissolving salts are lithium nitrate and thiourea in the different molar ratio of 0.5:2M, 1:2M and 1.5:2M in double distilled water at constant room temperature. The filtered solutions were distributed into different beakers (100 ml). The solution was stirred well for about 6 hours using a magnetic stirrer constantly.

The saturated solutions were filtered using Whattman filter paper. The filtered solutions were poured into different beaker and it is kept at a constant temperature bath maintained at room temperature in a dust free compartment for the slow evaporation process. The beaker was closed with a paper and the solution in the beakers was allowed to evaporate. After a few days small good optical transparent seed crystals are started growing in the beaker. After three weeks of growth colorless transparent crystals are obtained. Good shaped crystals were selected among the harvested crystal for the experimental studies.

Table 2.1: Optimized Growth Conditions of TuLiNO3 Crystals

Crystals	Growth Temperature	Period of Growth	Dimensions
$TuLiNO_3$ 0.5:2M	300K	25 to 30 days	7x7x4 mm^3
$TuLiNO_3$ 1.0:2M	300K	20 to 25 days	17x21x8 mm^3
$TuLiNO_3$ 1.5:2M	300K	20 to 25 days	14x8x7 mm^3

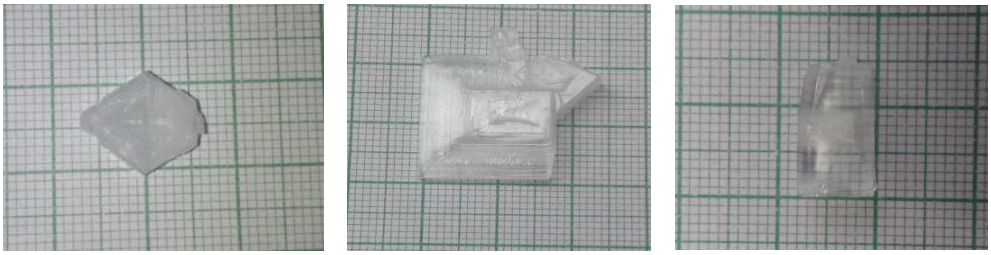


Figure 2.1: Photographs of Different Concentration of TuLiNO3 Crystals

3. RESULTS AND DISCUSSIONS

3.1. Single Crystal XRD Analysis

The Lithium nitrate doped thiourea crystal (1M: 2M) was subjected to Single X-ray diffraction studies using an ENRAF NONIUS CAD4 diffractometer with MoKα radiation (λ = 0.7173 Å) to determine the unit cell dimensions. The structure have been solved by the direct method and refined by the full matrix least square technique using SHELXL programme. It was found that $TiLiNO_3$ crystal belongs to orthorhombic system with a non-Centro symmetric space group $P2_12_12_1$. These results are suggested that the induction of their legend in the $TuLiNO_3$ crystals does not change the crystal system, though there is a small change in the lattice parameters.

Table 3.1: Unit Cell Parameters of TuLiNO3 Crystal

Lattice Parameter	Thiourea	Lithium Nitrate	$TuLiNO_3$
a (Å)	7.657	6.765	5.502
b (Å)	8.588	10.320	7.689
c (Å)	5.485	5.130	8.593
α°	90	90	90
β°	90	90	90
γ °	90	90	90
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma (62)	Cmcm (63)	$P2_12_12_1$
Volume ($Å^3$)	360	358.149	363.5

3.2. Powder XRD Analysis

In the present work, Powder X-ray diffraction pattern of the grown $TuLiNO_3$ crystal was recorded using EQUINOX-1000 model powder X-ray diffractometer with CuKα (λ = 1.540598 Å) radiation for structural analysis of the crystal. The ideal Specimen is a statistically infinite amount of randomly oriented powder with crystallite size less than 10

μm, mounted in a manner in which there is no preferred crystallite orientation. Finely crushed powder of the crystal has been used for its analysis. The sample was scanned within the assortment of 10-80° in a scanning speed of 1°/min. The intensity of the diffracted beam was listed as a part of 2θ along with the peaks have been clicked XRD pattern for the crystal is displayed at the Figure 3.1. The lattice parameters and cell volume values for the doped crystals are given in **Table 3.2**.

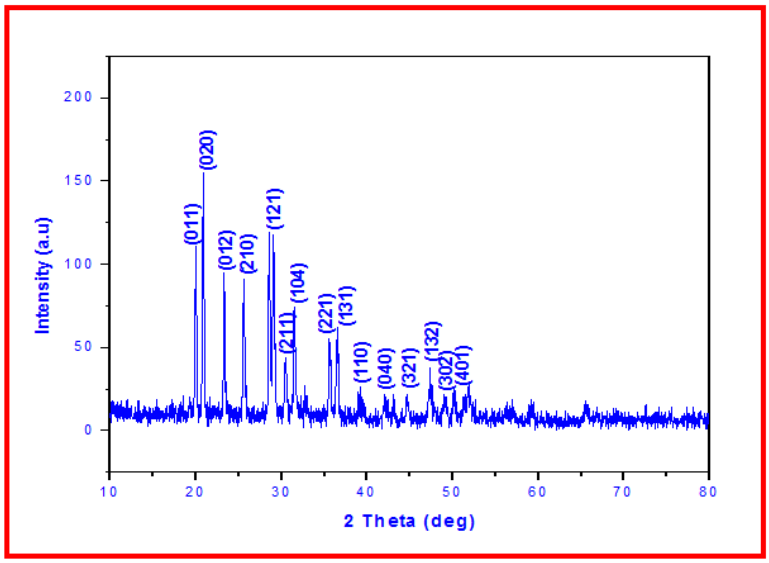


Figure 3.1: Powder XRD pattern of TuLiNO3 crystal (1M: 2M)

Table 3.2: Powder XRD Data of TuLiNO3 Crystal

[˚2 Theta]		d-Spacing [Å]		(h k l)	References
Observed Value	Standard Value	Observed Value	Standard Value		
19.951	19.185	4.621	4.622	011	JCPDS Card No. 83-2252 80-0203
20.915	20.668	4.293	4.294	020	
24.434	24.821	3.613	3.584	012	
25.452	25.452	3.485	3.496	210	
28.627	28.842	3.076	3.093	131	
30.555	30.288	2.943	2.948	211	
32.856	32.210	2.767	2.776	104	
35.478	35.339	2.529	2.537	221	
36.899	36.304	2.493	2.472	110	
38.827	38.337	2.352	2.346	132	
42.092	42.051	2.157	2.147	040	
44.797	44.437	2.094	2.037	321	
47.472	47.378	1.919	1.917	132	
48.840	48.696	1.873	1.868	302	
50.177	50.454	1.791	1.807	401	

3.3. Fourier Transform Infrared (FTIR) Analysis

The FTIR analysis of lithium nitrate doped thiourea in different molar ratio (0.5M : 2M, 1M :2M and 1.5M :2M) of crystals were carried out in the region of 4000-400 cm^{-1} using SHIMADZU-8400 with a resolution of 4 cm^{-1}. **Figure 3.2** show the FT-IR spectrum of $TuLiNO_3$ crystals. Other important functional groups are detailed in **Table 3.3**.

Table 3.3: Vibrational Assignments of Lithium Nitrate Doped Thiourea Crystals

Crystal	Wavenumber (cm^{-1})	Assignments
$TuLiNO_3$	3414, 3400 and 3380	Asymmetric-H_2O(O-H) Stretching
	2360, 2355 and 2350	NH_3 stretching
	1636, 1617 and 1607	Symmetric NO_3 stretching
	1468, 1458 and 1449	NH_2 bending
	1100, 1108 and 1120	Asymmetric N-C-N stretching
	892	C-N stretching
	832	C-H bending
	825	NO_3 stretching
	731	Symmetric C=S stretching
	500	COO^-, C-N stretching
	466	Symmetric N-C-N bending

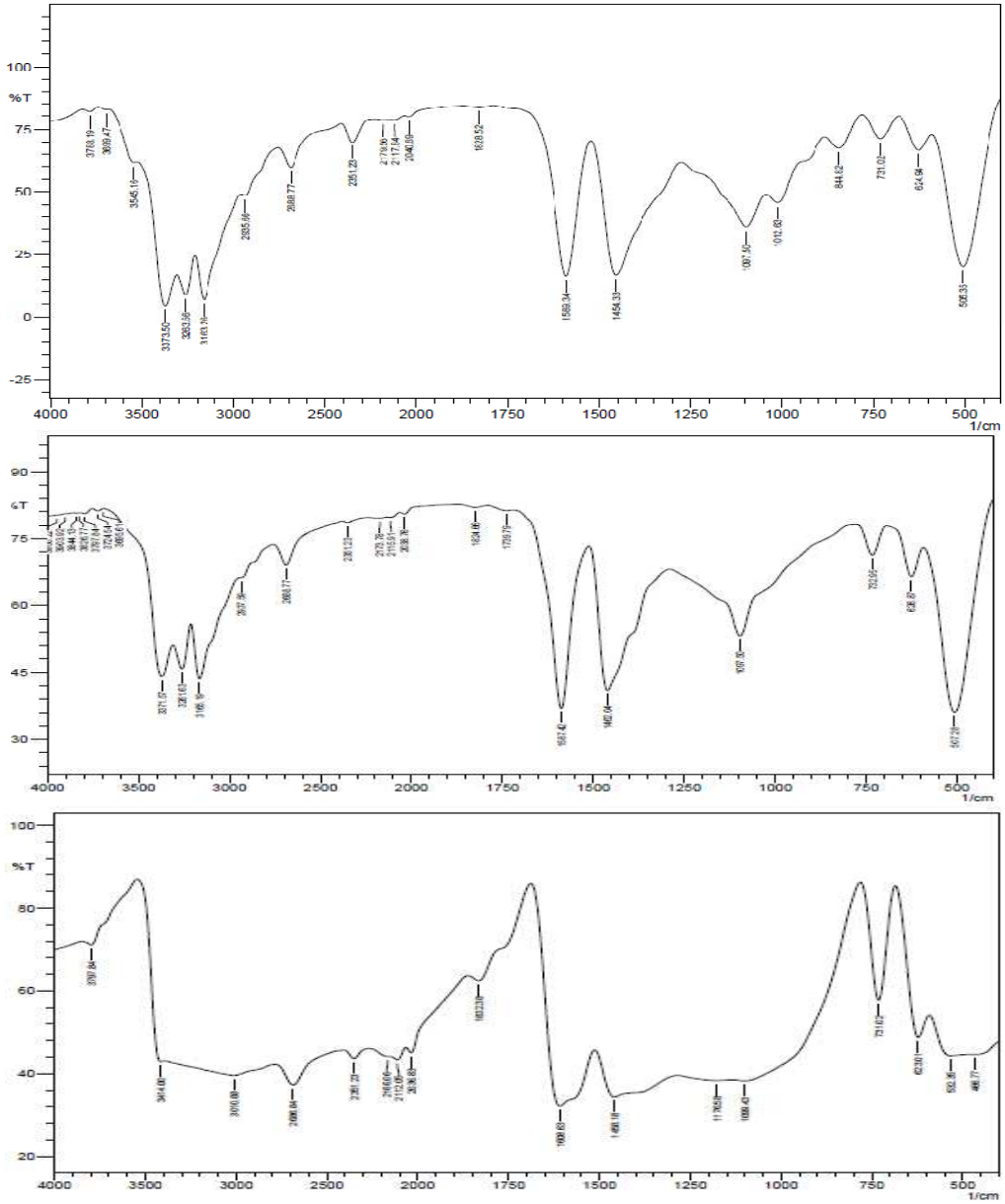
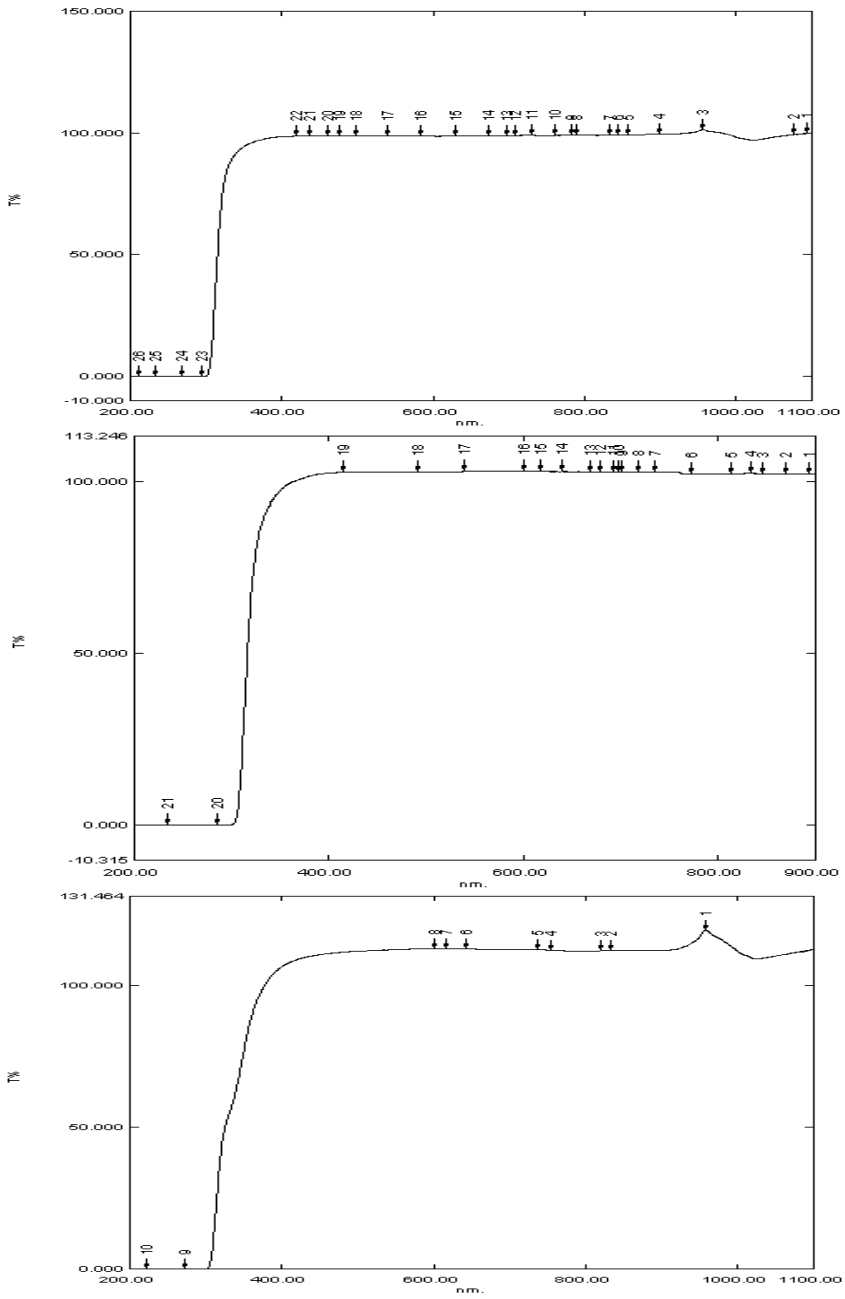


Figure 3.2: FT-IR Spectrum of TuLiNO3 Crystals for Different Molar Ratio (a, b and c)

3.4. UV-Vis- NIR Study Analysis



Figures 3.3: UV-Vis Spectrum of TuLiNO3 Crystals for Different Molar Ratio (a, b and c)

UV-Vis-NIR spectral study is a useful tool to determine the transparent for a material to be optically active. The optically transmission spectrum of lithium nitrate doped thiourea in different molar ratio (0.5M:2M, 1M:2M and 1.5M:2M) of crystals were recorded in the range 200 -1100 nm by shimadzu - UV1800 spectrophotometer at room temperature.

It covers a broad region near ultraviolet (200nm to 400nm), visible (400nm to 800nm) and far infrared (800nm to 1100nm). The observed plot of transmittance (%) Vs wavelength (nm) is shown in **Figure 3.3**. At lower cutoff wavelength 285 nm, a sharp fall of transmission to zero was observed, indicating a single transmission in the near UV region thiourea. From the value of fundamental absorption wavelength, the band gap energy of the material is calculated using the formula,

$Eg = hc / \lambda$ (eV); $Eg = 4.36$ eV

3.5. Second Harmonic Generation Studies

To be able to locate the SHG, the crystals have been ground with a version to the Kurtz and Perry method into powder (roughly 70μm) and densely packed between 2 translucent microscope glass slides. After the samples are put on the glass slides, aQ - Switched style Nd:YAG Quanta beam series laser of 1064 nm, creating an 8 ns pulse and functioning in 6mJ/pulse and in a speed of 10 Hz, is pumped in the appropriate angle and distance so as to see clearly the SHG from the green color area (532 nm), the anticipated emitted half wavelength indicate.

The second harmonic signals generated in the crystalline sample were confirmed from emission of green radiation by the sample. The SHG efficiency of the $TuLiNO_3$ Crystal for different molar ratio (0.5:2M, 1.0:2M and 1.5:2M) was evaluated by taking the microcrystalline powder of KDP as the reference material. The second harmonic signal for KDP is 8.8 mJ. The powder SHG efficiency output was found to be 0.73 times greater with respect to KDP. The NLO conversion relative efficiency of thiourea lithium nitrate crystals was presented in **Table 3.4.**

Table 3.4: SHG Efficiency of the TuLiNO3 Crystal

No. of Samples	Samples, Code Name	NLO efficiency Output Power (mJ)	Relative Efficiency
	KDP (Reference Standard)	8.8	1.00
1.	$TuLiNO_3$ 0.5:2M	5.9	0.67
2.	$TuLiNO_3$ 1.0:2M	6.2	0.70
3.	$TuLiNO_3$ 1.5:2M	6.4	0.73

3.6. Thermal Analysis

Thermal analysis is a very essential method to study the thermal behaviour of materials and finds widespread applications in diverse industrial and research fields. The TG-DTA measurements were performed in nitrogen atmosphere at a heating rate of 20 $^{\circ}$C/min for the temperature range of 30-1100 $^{\circ}$C using STA-500 simultaneous thermal analyzer,

The lithium nitrate doped thiourea crystal (0.5:2M, 1.0:2M and 1.5:2M) samples shows a thermal stability of the material 210 $^{\circ}$C and there is no weight loss occurs. From TGA analysis curves, the maximum rates of degradation were at different temperatures and the second degradation step was indefinite. The onset points for the starting point of the $TuLiNO_3$ crystals were at 222 °C, 215 °C and 210 °C respectively.

The DTA spectra of TuLiNO3 crystal Signify an endothermic transition round 200 °C and an exothermic one at roughly 250 °C. This results reveal that the lithium ion samples reveal a significant endothermic transitions at 260 °C. TuLiNO3 indicates another endothermic transition in over 600 °C. In this temperature range, the potential NLO software become promising, as a result of usage of laser powers, demonstrating a fantastic performance below 250 °C.

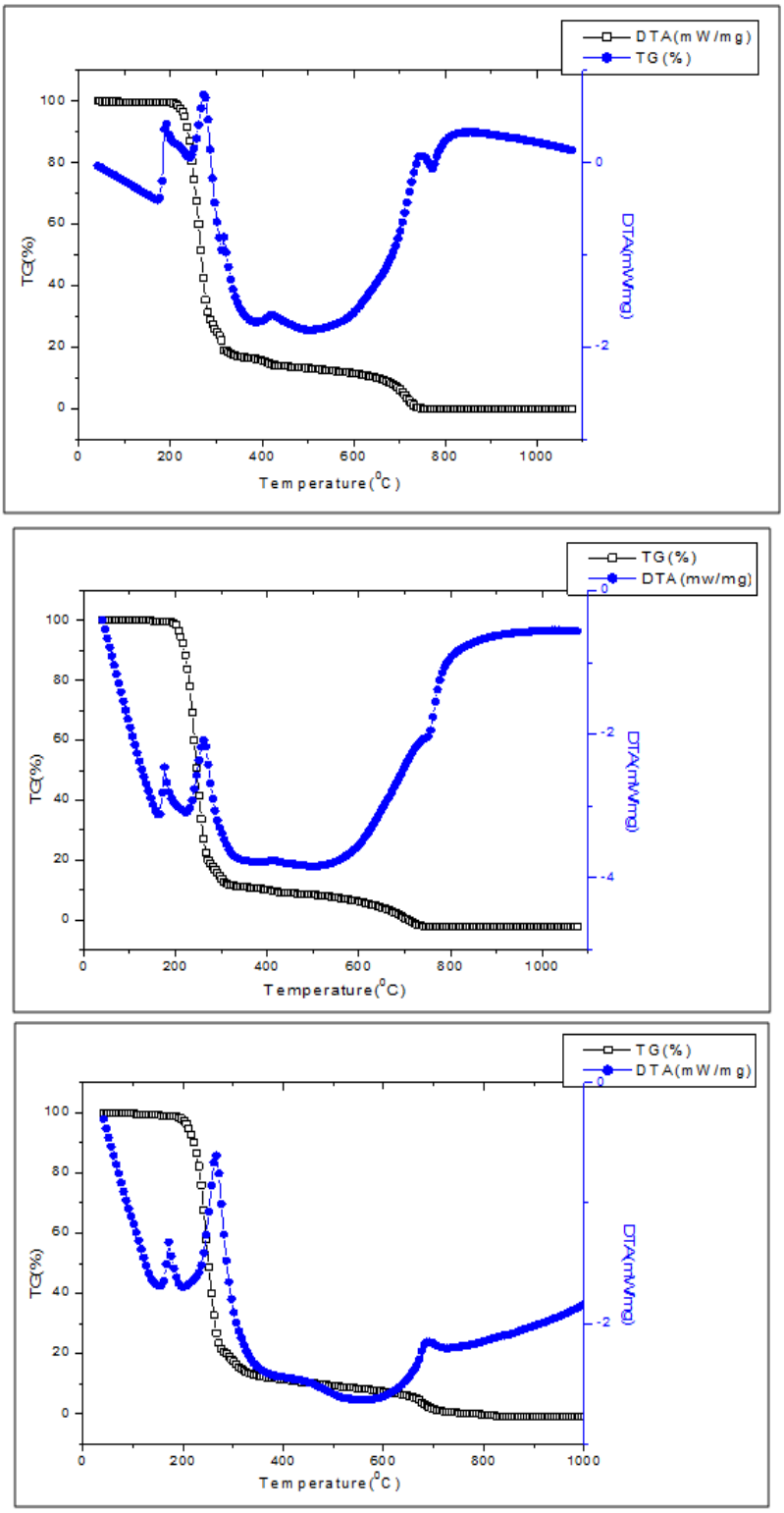


Figure 3.4: TG-DTA Curves of TuLiNO3 Crystals (0.5:2M, 1.0:2M and 1.5:2M)

4. CONCLUSIONS

The X-ray spectroscopic analysis of the doped specimen confirms the presence of lithium nitrate in the crystalline matrix of thiourea crystal. The lattice parameters were determined from the single crystal XRD and it has been found that $TuLiNO_3$ belongs to the orthorhombic crystal system. The sharply well defined Bragg's peak confirms the crystalline

nature of the grown $TuLiNO_3$ crystal. It was confirmed by powder XRD pattern. The FT-IR study confirms presence of the functional groups in the samples. The thermal stability observed for the lithium nitrate doping of Thiourea crystals to be found as 210 °C. The $TuLiNO_3$ crystal is melting point at 260 °C. The optical transparency and the lower cutoff wavelength at 285 nm were identified from the UV-Vis NIR spectrum. The powder SHG efficiency output was found to be 0.73 times greater with respect to KDP. The Kurtz and Perry powder technique shows that the crystal is a promising candidate for good optical and opto-electronic applications.

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